J. Mater. Environ. Sci. 7 (4) (2016) 1107-1118 *Abdallah et al.*
ISSN : 2028-2508
CODEN: JMESC

Corrosion Inhibition of Zinc in Hydrochloric Acid using some Antibiotic Drugs

M. Abdallah[a,b], I. A. Zaafarany[a], B.A. AL Jahdaly[a]

[a]*Chemistry Department, Faculty of Applied Sciences, Umm Al-Qura University, Makkah, Saudi Arabia.*
[b] *Chemistry Department, Faculty of Science, Benha University, Beha, Egypt*

Received12 Dec 2015, Revised 11 Feb 2016, Accepted 17 Feb 2016
**For correspondence: Email: metwally555@yahoo.com (M. Abdallah); Phone: +966580369045; Fax: +966 25270000*

Abstract
The effect of some antibiotic drugs, namely, paromomycin, streptomycin and spectinomycin on the corrosion behavior of zinc in 1.0MHCl solutions was investigated using potentiodynamic polarization, electrochemical impedance (EIS) and weight loss techniques. The percentage inhibition efficiency was found to increase with increasing drug concentration and with decreasing temperature. Potentiodynamic polarization curves proved that the studied antibiotic compounds acted as mixed type inhibitors. The inhibiting effect of these compounds was interpreted in view of its horizontal adsorption on the Zn surface through the active centers contained in their structure. The adsorption process obeys Temkin isotherm. Some activated thermodynamic parameters were calculated and interpreted. All EIS curves exhibitone capacitive loop indicating the corrosion process is controlled by charge transfer process.

Keywords: Zinc, Antibiotic drugs, Corrosion inhibitors, Adsorption, EIS

1. Introduction
Zinc metal is highly susceptible to attack by acids. For scale removal and cleaning of zinc surfaces with acidic solution [1]. The use of inhibitors is one of the most practical methods for protection of zinc against corrosion arising from the use of hydrochloric acid. Some organic compounds have been used as corrosion inhibitors for dissolution of zinc electrode in hydrochloric acid [2-12]. These compounds are adsorbed at the metal surface and they block the active site and consequently, decreasing the corrosion rate and consequently increase the inhibition efficiency [13]. The strength of adsorption process depends on the chemical structure of the inhibitors and its prosperities such as aromaticity, functional groups, electron density of the donor atoms-orbital's characters of donating electrons and the number of aromatic rings [14].

Most of organic inhibitors are toxic to the environment and increasing awareness of health and ecological risks, .Attention is being drawn towards finding highly efficient, cheaper and nontoxic inhibitors. There are a few manuscripts used the pharmaceutical drugs as save corrosion inhibitors to inhibit the corrosion of metals and alloys in the literature. In previous work, rhodanine azosulpha drugs [15], are used for inhibiting the corrosion of 304 stainless steel in hydrochloric acid solution, anti-bacterial drug [16] inhibit the corrosion of aluminum in hydrochloric acid solution, antihypertensive drugs [17] inhibit the corrosion of aluminum and aluminum silicon alloys in aqueous solutions and antibacterial cephalosporin [18] inhibit the corrosion of iron in

hydrochloric acid solutions. Some antibiotic drugs, namely, gentamicin, kanamycin, amikacin are used as inhibitors for aluminum corrosion in 1.0 M HCl solution [19]. The inhibiting action of these types of drugs due to the parallel adsorption of these compounds on the surface of the metal is due to the presence of more than one active center in the inhibitor molecule.

The objective of the present work is to investigate the inhibiting effect of some antibiotic drugs toward the corrosion of Zn in1.0M HCl solution using potentiodyamic polarization, electrochemical impedance spectroscopy (EIS) and weight loss techniques. The effect of increasing temperature on the corrosion of Zn in 1.0 M HCl solution containing 500 ppm of antibiotic drugs was studied and some thermodynamic parameters of activation were calculated and discussed.

2. Experimental techniques

The working zinc electrode used in this study having purity 99. 99%. For weight loss measurements the test Zn sheets having dimension 1.0x 1.0 x 0.2cm^3. The sheets were first polished with different grades of emery paper in order to obtain a smooth surface and then degreasing with acetone and then rinsed with bidistilled water, dried between two filter papers. The procedure methods of weight loss measurements were carried out as described elsewhere [20].

The potentiodynamic polarization measurements were carried out using a PS remote potentiostat with PS6 software to calculate the corrosion parameters at a scanning rate 10mV/sec. The electrochemical impedance spectroscopy (EIS) technique was carried out in frequency ranges from 100 kHz to 10 mHz with amplitude of 5 mV peak-to-peak using ac signals at open circuit potential. EIS were controlled by SP-150 potentiostat/ galvanostate with 092-06/2Potentio.Galvano board with EIS option at 30 ± 1^{o}C.A three compartment cell with saturated calomel reference electrode (SCE) and a Pt foil as an auxiliary electrode was used. The potential was measured against a reference saturated calomel electrode (SCE). A cylindrical Zn rod embedded in Araldite with an exposed surface area of 0.56 cm^2 was used.

The Treatment of the electrode as described in the weight loss measurements. The experiments were carried out at 30 ±1^{o}C using air thermostat. Complete wetting of the surface was taken as an indication of its cleanliness. All chemicals used were of A.R. quality.

2.1. *Inhibitors*

The antibiotic drugs have been investigated purchased from Pfizer pharmaceuticals company Egypt. These compounds are given in Table 1.

3. Results and discussion

3.1. *Potentiodyamic polarization*

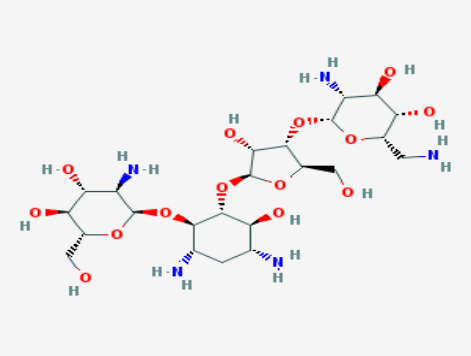
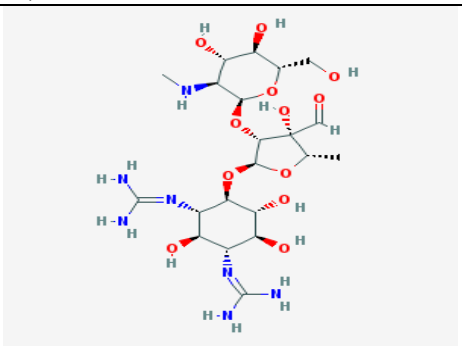
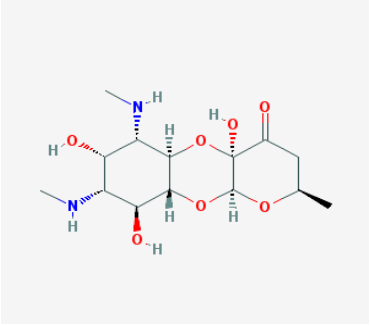
Figure 1 shows the potentiodyamic polarization curves of the zinc electrode in 1.0M HCl solution in the absence and presence of different concentrations of compound I at voltage scan rate 10 mV/sec and 30^{o}C.The same curves were obtained for the other compounds (II &III) not shown. Several corrosion parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic and cathodic Tafel slopes (β_a and β_c), and inhibition efficiency (% IE)are calculated and listed in Table2.

The percentage inhibition efficiency (% IE) was calculated using the following equation:

$$\%IE = \left(1 - \frac{I_{corr}}{I^{\circ}_{corr}}\right) x\,100 \qquad (1)$$

Where I°_{corr} and I_{corr} are the corrosion current densities in the absence and in the presence of the inhibitor.

Table 1: The chemical structure of antibiotic drugs

Compounds	**Structure**
Compound I **Paromomycin**	 Molecular formula: $C_{23}H_{45}N_5O_{14}$ Molecular mass: 615.63g/mol **IUPACname**:3*S*,4*R*,5*R*,6*S*)-5-amino-6-[(1*R*,2*S*,3*S*,4*R*,6*S*)-4,6-diamino-2-[(2*S*,3*R*,4*R*,5*R*)-4-[(2*R*,3*R*,4*R*,5*R*,6*S*)-3-amino-6-(aminomethyl)-4,5-dihydroxy-oxan-2-yl]oxy-3-hydroxy-5-(hydroxymethyl)oxolan-2-yl]oxy-3-hydroxy-cyclohexyl]oxy-2-(hydroxymethyl)oxane-3,4-diol
Compound II **Streptomycin**	 Molecular formula: $C_{21}H_{39}N_7O_{12}$ Molecular mass: 581.574 g/mol **IUPACname**:4-diguanidino-3,5,6-trihydroxy-cyclohexoxy)-4-[4,5-dihydroxy-6-(hydroxymethyl)-3-methylamino-tetrahydropyran-2-yl]oxy-3-hydroxy-2-methyl -tetrahydrofuran-3-carbaldehyde
Compound III **Spectinomycin**	 Molecular formula $C_{14}H_{24}N_2O_7$: Molecular mass: 332.35 g/mol **IUPACname**:3*S*,5*R*,8*R*,10*R*,11*S*,12*S*,13*R*,14*S*)-8,12,14-trihydroxy-5-methyl-11,13-*bis*(methylamino)-2,4,9-trioxatricyclo[8.4.0.0^{3,8}]tetradecan-7-one

Inspection of Table 2, it is obvious that, the presence of antibiotic compounds led to the corrosion potential is slightly shift towards the active direction in comparison to the result obtained in the absence of the inhibitor and the values of I_{corr} decreases in all the studied concentrations, indicating the inhibiting effect of these compounds. The values of anodic (β_a) and cathodic (β_c), Tafel slopes approximately unchanged in the presence of the inhibitors, indicating that these compounds are mixed type inhibitors. The antibiotic compounds acted by merely blocking the reaction sites of the metal surface without changing the anodic and cathodic reaction mechanisms [21]. The order inhibition efficiency of the investigated compounds decreases in the following order:
Compound I > Compound II > Compound III

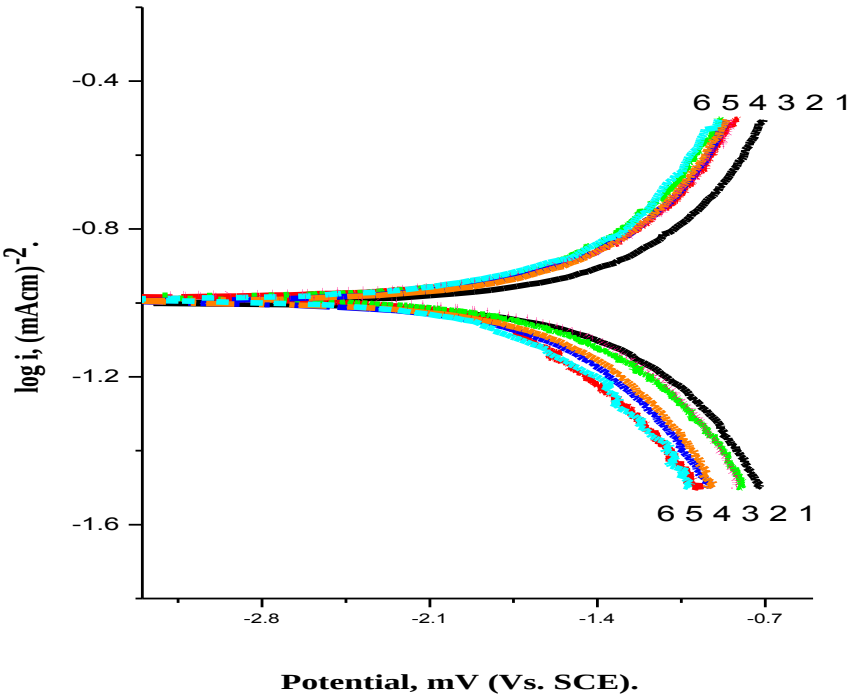


Figure 1: Potentiodynamic polarization curves for the corrosion of zinc electrode in 1M HCl in the absence and presence of different concentrations of compound I. 1) 0 ppm, 2) 100 ppm, 3) 200 ppm, 4) 300 ppm, 5) 400 ppm, 6) 500 ppm.

3.2.*Electrochemical impedance spectroscopy (EIS)*

The corrosion behavior of the zinc electrode in 1.0 M HCl solution in the absence and presence of different concentrations of the antibiotic compounds was investigated by the EIS method at 30°C. Fig.2 shows the Nyquist plots for zinc electrode in 1.0 M HCl solution in the absence and presence of different concentrations of compound I at 25°C as an example of the studied compounds. The same curves were obtained for the other compounds (II &III) not shown. It is obvious that the obtained Nyquist impedance diagrams in most cases do not show perfect semicircle, generally attributed to the frequency dispersion of interfacial impedance which arises due to surface roughness, impurities, dislocations, grain boundaries, adsorption of inhibitors, and formation of porous layers and in homogenates of the electrode surface [22-23]. The data reveal that, each impedance diagram consists of a large capacitive loop with the low frequency dispersion (inductive arc). This inductive arc is generally attributed to anodic adsorbed intermediates controlling the anodic process [24]. By following this, inductive arc was disregarded.

Table 2: Effect of increasing concentrations of antibiotic compounds on the corrosion kinetic parameters obtained from potentiodynamic polarization for the corrosion of zinc electrode in 1M HCl

System	Concentration M	$E_{corr.}$, mV(SCE)	$I_{corr.}$ μ A cm^{-2}	β_a mV dec^{-1}	β_c mV dec^{-1}	IE%
Blank	**0.0**	975	0.445	322	166	-
Compound 1	**100 ppm**	978	0.137	325	170	69.21
	200 ppm	981	0.085	328	174	80.89
	300 ppm	985	0.066	330	176	85.16
	400 ppm	990	0.042	332	178	90.56
	500 ppm	997	0.031	334	180	93.03
Compound 2	**100 ppm**	975	0.146	332	164	67.19
	200 ppm	979	0.094	335	168	78.87
	300 ppm	985	0.074	333	173	83.37
	400 ppm	988	0.048	338	175	89.21
	500 ppm	995	0.038	340	178	91.46
Compound 3	**100 ppm**	982	0.154	330	168	65.39
	200 ppm	986	0.108	333	172	75.73
	300 ppm	990	0.086	335	175	80.67
	400 ppm	994	0.057	336	178	87.19
	500 ppm	996	0.046	338	185	89.66

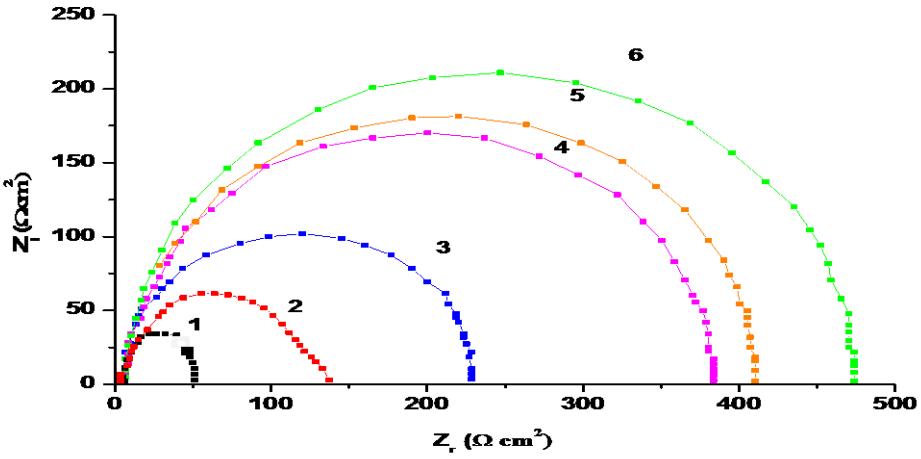


Figure 2: The Nyquist plots for the corrosion of zinc electrode in 1M HCl in absence and presence of different concentrations of compound I. 1) 0 ppm, 2) 100 ppm, 3) 200 ppm, 4) 300 ppm, 5) 400 ppm, 6) 500 ppm.

The impedance spectra of the Nyquist plots were analyzed by fitting the experimental data to a simple equivalent circuit model is given in Fig. 3, which includes the solution resistance R_s and the double layer capacitance C_{dl} which is placed in parallel to the charge transfer resistance R_{ct} [25].

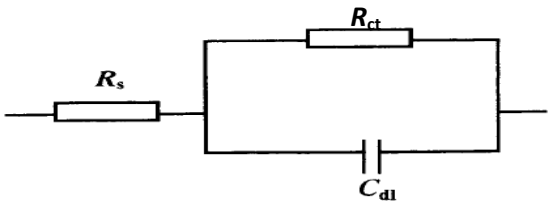


Figure 3: The equivalent circuit model used to fit the experimental results.

The impedance diagram shows the same trend (one capacitive loop), in the absence and presence of various concentrations of inhibitors, however, the diameter of this capacitive loop increases with increasing concentration.
The main parameters deduced from the analysis of Nyquist diagram are the resistance of charge transfer R_{ct} (diameter of the high frequency loop) and the capacity of double layer C_{dl}which is defined as:

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \quad (2)$$

The inhibition efficiencies obtained from the impedance measurements are defined by the following relations:

$$\%IE = \left(1 - \frac{R^{\circ}_{ct}}{R_{ct}}\right) x 100 \quad (3)$$

where R^{o}_{ct} and R_{ct} are the charge transfer resistance in the absence and presence of inhibitor respectively. The associated with the diagrams impedance are given in Table 3.

Table 3. Electrochemical parameter obtained by the EIS technique for the corrosion of zinc in 1.0 M HCl solution in the absence and presence of various concentrations of antibiotic compounds

System	Concentration M	R_s Ω cm²	R_{ct} Ω cm²	C_{dl} µF cm^{-2}	IE%
Blank	**0.0**	1.03	41	32.44	-
Compound 1	**100 ppm**	1.45	132	21.18	68.93
	200 ppm	1.82	220	16.22	81.36
	300 ppm	2.20	360	15.80	88.86
	400 ppm	2.86	422	13.15	90.28
	500 ppm	3.40	488	11.08	91.59
Compound II	**100 ppm**	1.42	121	18.46	66.11
	200 ppm	1.78	204	15.82	79.90
	300 ppm	1.85	266	14.79	84.58
	400 ppm	2.26	368	12.66	88.85
	500 ppm	2.68	406	10.88	89.90
Compound III	**100 ppm**	1.44	110	17.68	62.73
	200 ppm	1.72	148	15.43	72.29
	300 ppm	1.98	198	14.74	79.29
	400 ppm	2.20	304	12.81	86.51
	500 ppm	2.54	372	10.02	88.98

Inspection of Table 3, we conclude that, The values of R_{ct} increases with an increase in the concentration of the inhibitors indicating the formation of protective film on the metal-solution interface [26, 27]. The impedance diagram obtained has a semicircle appearance. This indicates that the corrosion of zinc in 1.0 M HCl is mainly controlled by a charge transfer process. The value of double layer capacitance (C_{dl}) decreases with increasing the inhibitor concentration due to the decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggested that these compounds function by adsorption at the metal solution/interface [7]. The order of inhibition efficiency of antibiotic drugs is as follows:

Compound I > Compound II> Compound III

3.3.*Weight loss measurement*

Figure 4 shows the weight loss-time curves for zinc sheets in 1.0 M HCl solution in the absence and presence of different concentrations of compound I. Similar curves were obtained for the other two compounds (II &III) not shown. As shown from this figure, by increasing the concentration of the additive, the weight loss of zinc sample is decreased. This means that the presence of these derivatives retards the corrosion of zinc 1.0 M HCl solution or in other words, these compounds act as an inhibitors. The linear variation of weight loss with time in uninhibited and inhibited 1.0 M HCl solution indicates the absence of insoluble surface films during corrosion. In the absence of any surface films, the inhibitors are first adsorbed onto the metal surface and thereafter impeding corrosion either by merely blocking the reaction sites (anodic and cathodic) or by altering the mechanism of the anodic and cathodic partial processes.

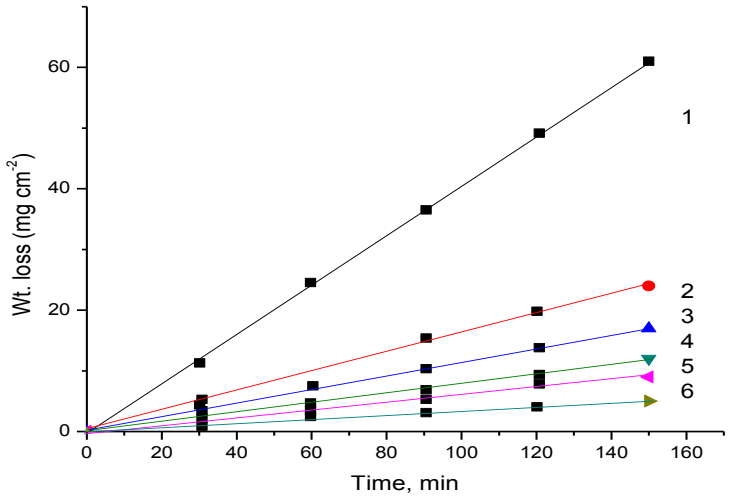


Figure 4: Weight loss-time curves for the corrosion of zinc electrode in 1M HCl in absence and presence of different concentrations of compound I. 1) 0 ppm, 2) 100 ppm, 3) 200 ppm, 4) 300 ppm, 5) 400 ppm, 6) 500 ppm.

Some corrosion from the weight loss measurements such as, the corrosion rate (R_{corr}), Thepercentage inhibition efficiency (%IE) and the surface coverage(θ) of the selected antibiotic compounds was computed using the following equations [28,29] and listed in table 4:

$$R_{corr} = \frac{\Delta W}{At} \quad (4)$$

$$\theta = \frac{R_{corr.free} - R_{corr.inh}}{R_{corr.free}} \quad (5)$$

$$\%IE = \frac{R_{corr.free} - R_{corr.inh}}{R_{corr.free}} x100 \quad (6)$$

where, (ΔW) is the difference in the weight loss of zinc sheets before and after immersing in the test inhibiting solution, $R_{corrfree}$ and $R_{corr.add}$represents the corrosion rate of the Zn in1.0 M HCl solution devoid of containing different concentrations of the antibiotic drugs respectively,(t) is the time in hours and (A)is the surface area in cm^2 .

Inspection of table 4, it is clear that the values of R_{corr} decrease and the values of % IE increase, indicating the inhibiting effect of the studied antibiotic compounds and decreases in the following order:

Compound I > Compound II> Compound III

This order will be discussed later.

The %IE obtained from the weight loss measurements are close to those deduced from potentiodynamic polarization and EIS methods.

Table 4: Effect of antibiotic drug concentration on the rate of corrosion (R_{corr}), the percentage inhibition efficiency (%I.E) and surface coverage (θ) obtained from weight loss measurements for corrosion of Zn Coupons in 1.0M HCl solution.

System	Concentration M	$R_{corr.}$ $mg.cm^{-2}.min.^{-1}$	IE%	θ
Blank	**0.0**	0.398	-	-
Compound 1	**100 ppm**	0.128	67.84	0.678
	200 ppm	0.095	76.13	0.761
	300 ppm	0.072	81.91	0.819
	400 ppm	0.048	87.94	0.879
	500 ppm	0.032	91.96	0.919
Compound II	**100 ppm**	0.139	65.07	0.651
	200 ppm	0.091	77.13	0.771
	300 ppm	0.067	83.16	0.832
	400 ppm	0.052	86.93	0.869
	500 ppm	0.037	90.70	0.907
Compound III	**100 ppm**	0.148	62.81	0.628
	200 ppm	0.102	74.37	0.744
	300 ppm	0.072	81.91	0.819
	400 ppm	0.064	83.92	0.839
	500 ppm	0.046	88.44	0.884

3.4.*Effect of temperature and activation parameters*

The effect of increasing temperature on the weight loss of zinc in 1.0 M HCl solution was studied at a temperature range (30 - 60°C) in the absence and presence of 500 ppm of the three antibiotic compounds. Similar curves in figure 4 were obtained not shown. It is clear that, the corrosion rate increases indicating the inhibition efficiency of the additives decreases with the rise in temperature and the desorption is aided. This behavior proves that the inhibition of zinc dissolution occurs through physical adsorption of the additives on the metal surface. Some activation thermodynamic parameters such as the activation energy Ea*, the enthalpy of activation ΔH^* and the entropy of activation ΔS^* for the

corrosion of Zinc sheets in 1.0M HCl solutions in the absence and presence of 500 ppm of the studied three drug compounds were calculated from the Arrhenius equation [30,31]:

$$R_{corr} = A\exp\frac{-E_a^*}{RT} \quad (7)$$

$$\log R_{corr} = \frac{-E_a^*}{2.303RT} + \log A \quad (8)$$

and transition – state equation :

$$R_{corr} = \frac{RT}{Nh}\exp\frac{\Delta S^*}{R}\exp\frac{-\Delta H^*}{RT} \quad (9)$$

where A is the frequency factor, h is the Planck's constant, N is Avogadro's number and R is the universal gas constant.

Figure 5 represents the relation between log R_{corr} and 1/T for zinc in 1.0 M HCl solution in the absence and presence of 500 ppm of the studied antibiotic compounds. A straight lines were obtained with slope equal to $-E_a^*/ 2.303R$. The calculated values of E_a obtained from the slope of the straight line are equal to 46.6kJ mol^{-1} in 1M HCl and equal 58.8, 54.8.5 and 50.7 kJ mol^{-1} for compounds I, II and III, respectively. The increase in the value of E_a in the presence of antibiotic drugs indicating a strong adsorption of the inhibitor molecules on the Zn surface. The presence of inhibitors induces an energy barrier for the corrosion reaction and this barrier increases with increasing the concentration of these compounds.

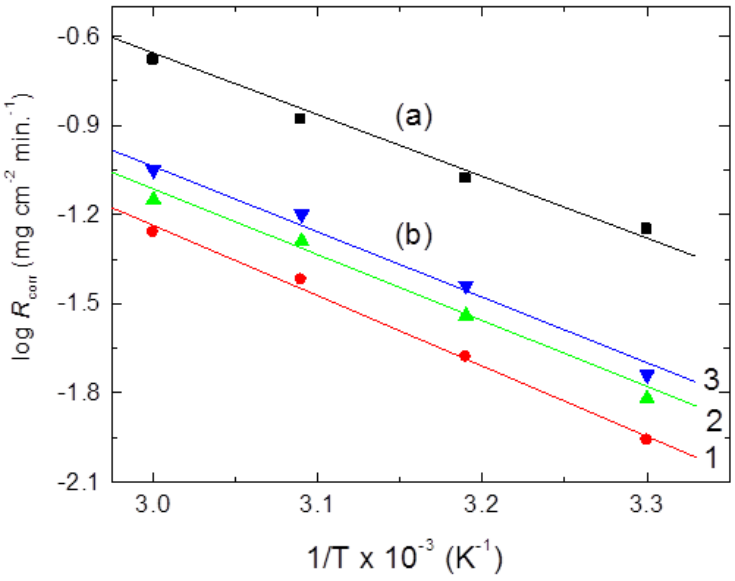


Figure 5: Log R_{corr}. vs. 1/T curves for Zn corrosion in 1.0 M HCl solution in the absence and presence of different concentrations of compound I.

Figure 6 represents the plot log (R_{corr} /T) vs. 1/T for zinc in 1.0 M HCl solution in the absence and presence of 500 ppm of the studied antibiotic compounds. A straight line was obtained with slope equal with slopes of ΔH^* / 2.303 R and the intercepts equal to log R/Nh + ΔS^* / 2.303R

The calculated values of enthalpy of activation ΔH^* are equal to 56.35kJ mol^{-1} in 1.0M HCl and equal to 60.83, 66.84 and 71.33 kJ mol^{-1} for compounds I, II and III, respectively. The positive values of ΔH^*reflect the endothermic behavior of antibiotic compounds on the Zn surface. Such behavior could be assigned to the presence of an energy barrier to the corrosion process due to the existence of these additives i.e., the process of adsorption exhibits a rise in the enthalpy of the corrosion process. The calculated values of the entropy of activation $\Delta S^*$are equal to -35.2 $Jmol^{-1}K^{-1}$ in 1.0M HCl solution and equal to -50.42, -46,38 and -41.48$Jmol^{-1}K^{-1}$for compounds I, II and III, respectively. The negative values of ΔS^*support the high absorbability of the antibiotic compounds on the Zn surface .This implies that the activated complex in the rate-determining step represents an association rather than dissociation step, meaning that the decrease in disordering takes place on going from reactants to the activated complex [32]. The order of the percentage inhibition efficiency of antibiotic compounds as gathered from the increase in E_a^* and ΔH^* values and decrease in ΔS^*values is as follows :

Compound I > Compound II > Compound III

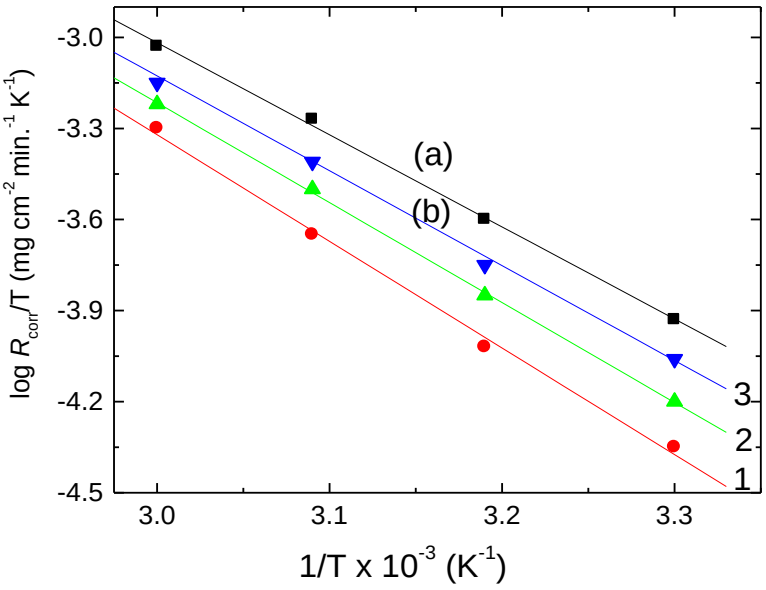


Figure 6: Log ($R_{corr.}$/T) vs. 1/T curves for Zn corrosion in 1.0 M HCl in the absence and presence of different concentrations of compound I.

3.5. *Adsorption isotherm and mechanism of inhibition*

Antibiotic compounds like organic additives inhibit the corrosion process by the adsorption on metal surface. Theoretically, the adsorption process can be regarded as a single substitution process in which an inhibitor molecule, I, in the aqueous phase substitutes an "x" number of water molecules adsorbed on the metal surface [33] vis:

$$I_{(aq)} + xH_2O_{(sur)} \longrightarrow I_{(sur)} + xH_2O_{(aq)} \quad (10)$$

Where, x is known as the size ratio and simply equals the number of adsorbed water molecules replaced by a single inhibitor molecule. The adsorption depends on the structure of the inhibitor, the type of the metal and the nature of its surface, the nature of the corrosion medium and its pH value, the temperature and the electrochemical potential of the metal-solution interface. Also, the adsorption provides information about the interaction between the adsorbed molecules themselves as well as their interaction with the metal surface.

The inhibiting effect of antibiotic compounds depending on the chemical structure of the antibiotic compounds . The presence of more than one active center in the chemical structure of inhibitors facilitates the interaction of the inhibitors with the Zn surface. It is expected that the horizontal adsorption of such compounds on the surface of zinc .The order of the percentage of inhibition efficiency of the three different techniques used are related to the molecular mass of the antibiotic compounds. So the compound I have the high inhibition efficiency more than compound II and compound III.A number of mathematical relationships for the adsorption isotherms including Langmuir, Freundlich, Frumkin, Temkin have been suggested to fit the experimental data of the present work. The best results were obtained fitted Temkin isotherm according to the following equation:

$$\ln K_C = a\theta \qquad (11)$$

Where, K is the equilibrium constant of the adsorption reaction, C is the inhibitor concentration in the bulk of the solution, a is the interaction parameter and θ is the surface coverage.

Figure 7 shows the plots of θ vs.log C (Temkin adsorption plots) for adsorption of additives on the zinc surface in M 1.0M HCl acid at 30°C .The data gave straight lines indicating that the adsorption of antibiotic compounds on the zinc surface obeys Temkin isotherm. Temkin isotherm is applied in the ideal case of physical and chemical adsorption on a smooth surface with no interaction between the adsorbed molecules.

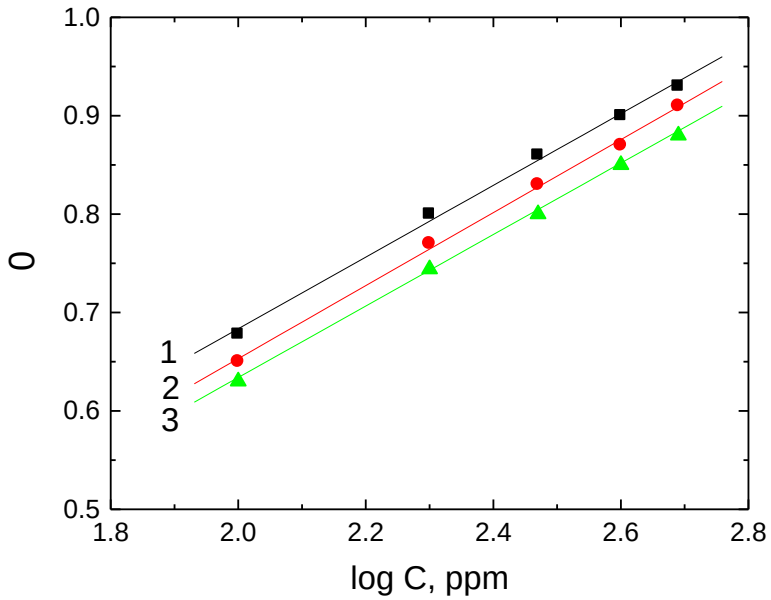


Figure 7: Temkin adsorption isotherm

Conclusions

1. The studied antibiotic compounds are effective inhibitors of corrosion of Zn electrode in 1.0 M HCl solution.
2. The potentiodynamic polarization measurements proved that the three compounds were mixed type inhibitors in 1.0 M HCl
3. The adsorption of the antibiotic compounds on the Zn surface obeys Temin isotherm.
4. It is proposed that the studied inhibitors horizontally adsorb on the Zn Surface forming a barrier between the electrode surface and the corrosion medium.

5- The corrosion reaction is controlled by charge transfer process as revealed from EIS results.

References

1. Agrawal Y.K., Talati J.D., Shah. M.D., Desai. M.N. Shah. N.K., *Corros. Sci.*, 46 (2004) 633.
2. Abdallah M., *Corros. Sci*. 45 (12), (2003) 2705.
3.Abdallah M., El-Etre A.Y., Moustafa M. F., *Portug. ElectrochimActa*,27 (2009) 615.
4. Fouda A.S., Abdallah .M., Atwa S.T., Salem M.M.**,** *Modern Applied Science, Canda*, 4 (12) (2010) 41.
5. Suedilen F., Robert F., Roosn C., Lebrini M., *Electrochim. Acta*, 133 (2014) 631.
6. Abdallah M., El-Etre A.Y., Moustafa M. F., *Protec. Met. Phys. Chem. Surf.*, 47 (2) (2011) 246.
7. Abdallah M., Zaafarany I., FoudaA.S., Abd El-Kader .D., *J. Mater Eng Performance*, 21(6) (2012) 995.
8. Stupnisek-Lisac E., PodbrscekS., *J. Appl. Electrochem.*,24 (1994) 779.
9. Abdallah M., Atwa S.T., Salem M.M., Fouda A.S., *Int. J. Electrochem. Sci.*, 8 (7) (2013) 10001..
10. Deyab M. A., *J. Power Sources*, 292, (2015) 66
11. Abdallah M., Zaafarany I., FoudaA.S., El-NagarW., *J. Electrochem. Plating Technology*, (2014) 2.
12. Abdallah M., Hazazi O.A., Al Jahdaly B.A., Fouda A. S., El-Nagar W., *Int. J. Innov. Research in Sci. Eng. Tech.* 3 (2014) 13802.
13. Hegazy M.A., Abdallah M., Awad M.K., Rezk M., Part I: Experimental Results, *Corros. Sci.*, 81 (2014) 54
14. Abdallah M., Moustafa M.E., *Annali Di Chimica*, 94 ((2004) 601.
15. Abdallah M., *Corros. Sci.*, 44 (2002) 717.
16. Abdallah M., *Corros.Sci.*, 46(8) 1981 (2004)
17. Abdallah M. Zaafarany I., Al-Karanee S.O., Abd El-Fattah A.A., *Arab. J. Chem.*, 5(2) (2010) 225.
18. Abdallah M., Zaafarany I., Al-Fahemi J.H., Abdallah Y., Fouda A.S., *Int. J. Electrochem. Soc.*,7 (2012) 6622
19. Abdallah M., AL Jahdaly B.A., *Int. J. Electrochem Sci***.,** 10 (2015*)* 9808-9823.
20. Mathur P. B., Vasudevan T., *Corrosion*, 38 (1982) 17.
21. Hazzazi O.A., AbdallahM., Gad E.A.M., *Int. J. Electrochem. Sci.*, 9 (2014) 2237
22. Bayol E., Kayakirilmaz K., Erbil M. , *Mater. Chem. Phys*., 104 (2007) 74.
23. Benalli O., Larabi L., Traisnel M., Gengembra L., Harek Y., *Appl. Surf. Sci.*, 253 (2007) 6130.
24. Mansfeld F., Jeanjaquest S.L., Kending M.W., *Corros. Sci.*, 26 (1986) 735.
25.Sekine I., Sabongi M., Hagiuda H., OshibeT., Yuasa M., Imahc T., Shibata Y., Wake T., *J. Electrochem. Soc*., 139 (1992) 3167.
26. Bentiss F., Traisnel M., Lagrenee M., *Corros.Sci.* ,42 (2000) 127.
27. Murlidharan S., Phani K.L.N, Pitchumani S., RavichandranS., *J. Electrochem. Soc.*, 142 (1995) 1478.
28. Tang L.B., Mu G., Liu G., Corros. Sci. 45 (2003) 2251.
29. Hegazy M.A.,Abdallah M., Ahmed H., *Corros. Sci.* 52 (2010) 2897.
30. Riggs O.L., Hurd R. M., *Corrosion*, 23 (1967) 252.
31. Laider K.J., *Chemical Kinetics*, McGraw Hill Publishing Company Ltd (1965)
32. Fouda A.S., Al-Sarawy A.A., El-Katori E.E., *Desalination*, 201 (2006) 1.
33. Fouda A.S., Farahat M., Abdallah M., *Res. Chem. Intermed*, 40 (2014) 1249.